IS SILICON A LIGHT COMPONENT IN THE EARTH'S CORE? - CONSTRAINTS FROM LIQUID METAL - LIQUID SILICATE PARTITIONING OF SOME LITHOPHILE ELEMENTS. U. Mann[1], D.J. Frost[1], D.C. Rubie[1,2], C.K. Shearer[2], C.B. Agee[2], [1]Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany, ute.mann@uni-bayreuth.de, [2]Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, USA.

Introduction: Heterogeneous models of core formation in the Earth are based on a stepwise increase in oxidation state during accretion resulting from a stepwise change in the composition of the accreting material [1, 2]. The initial stage is assumed to have been quite reducing, resulting not only in the extraction of relatively siderophile but also of several weakly siderophile and lithophile elements from the Earth's mantle into the core. This could explain the apparent depletion of Si and thus support the CI chondrite Earth model [3] in which Si (~7 wt%) is proposed to be the principal light element in the Earth core. On the other hand there are certain lithophile elements that are not at all depleted in today's Earth's mantle, such as Ta, or that are only depleted due to volatility but not by core formation as in case of Ga, In and Zn. Studying their metal-silicate partitioning behaviour enables us to place constraints on the initial very reducing stage of such heterogeneous accretion models. The lower limit for the oxidation state can be set where these elements become more siderophile than elements, such as Si, that are weakly depleted. So far only few HP /HT experimental data for such elements are available. However, simple thermodynamic calculations suggest that the behavior of Ta should be very similar to that of Si and thus imply that it could become siderophile at very low oxygen fugacities.

Experimental Procedure: In order to investigate the liquid metal-liquid silicate partitioning behaviour of Ta, Ga, In and Zn, we have performed multi-anvil-experiments over a pressure range of 6 - 20 GPa, at temperatures between 2100 -2400°C and a range of redox conditions below IW. In each experiment the starting material was a mixture of 56 wt% of synthetic primitive mantle composition and 40 wt% of Fe-alloy and doped with 4 wt% of the investigated elements (as oxides). The metallic component always contained 2 wt% Ni and 1 wt% Co and was mixed from varying proportions of Fe powder and $Fe_{84}Si_{16}$ or $Fe_{71}Si_{29}$. The amount of Si metal was adjusted in order to achieve a range of redox conditions. Graphite and MgO single crystal capsules were employed to contain the samples.

At high temperature, liquid metal and liquid silicate separated from each other with the metal forming a discrete blob. Both metal and silicate phases were analyzed with EMP using a defocused electron beam as in both cases heterogeneous quench textures had developed. At the extreme ends of the studied redox range, trace element concentrations are very low in one of the phases. In such cases, secondary ion mass spectrometry has been employed for preliminary analyses of the quenched silicate liquid. These measurements were made using a Cameca ims 4f ion microprobe in the Institute of Meteoritics at the University of New Mexico. An O- primary beam was used, operating at 10 kV. A primary beam current of 25 nA resulted in a spot size of ~25-30 µm. Isobaric interferences were minimized by energy filtering the secondary beam using a voltage offset of 105 V, and an energy window of ± 25 V. Glass standards were used to define appropriate calibration curves.

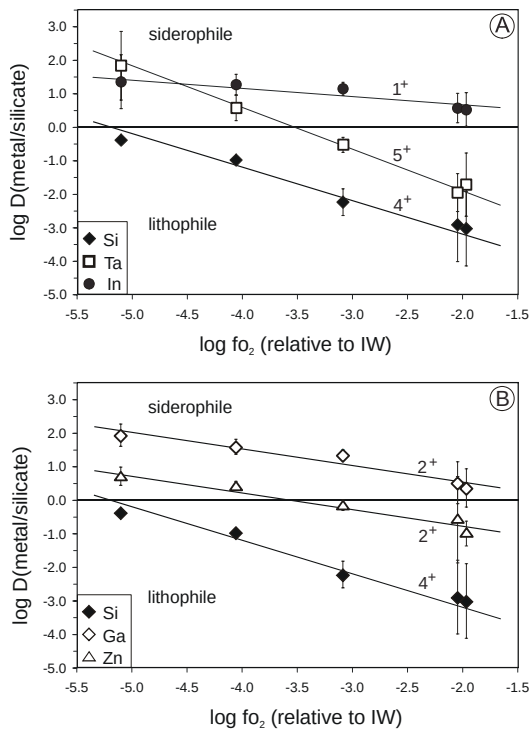

Fig. 1: Metal-silicate partitioning behavior of (A) Si, Ta, In and (B) Ga and Zn at 6GPa, 2100°C. For each element the slopes of the correlation trend give an estimate for its valence state.

Results: Metal-silicate partition coefficients (D) for Si, Ta, Ga, In and Zn, obtained at 6 GPa and 2100°C, are plotted against logarithmic values of oxy-

gen fugacity in Fig. 1. The oxygen fugacity was calculated relative to the iron-wüstite buffer (IW) from the Fe - FeO equilibrium between metal and silicate phase.

For all these elements there is a linear correlation between log D and log fo_2. Among them, Si is the least siderophile element and maintains its lithophile character over the entire investigated redox range. However, even under these conditions some depletion of Si from the mantle could take place. Ga and In on the other hand are always siderophile. A comparison of Si with Ta shows that over the entire redox range Ta has a more siderophile character than Si and therefore would have been strongly depleted at any conditions under which significant Si has partitioned into the core

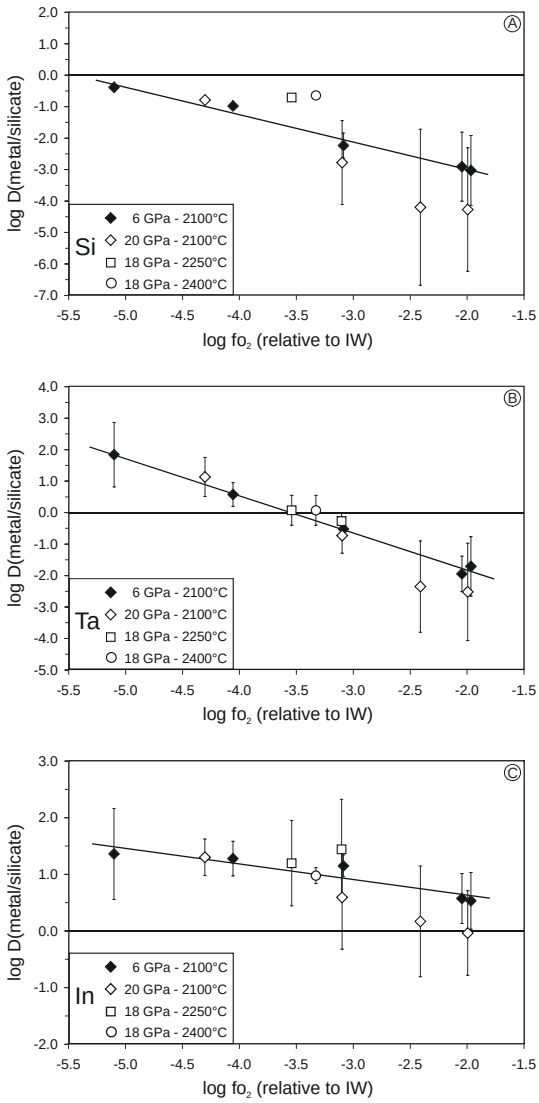

Fig. 2: Influence of pressure and temperature on the metal-silicate partitioning behaviour of (A) Si, (B) Ta and (C) In.

Plots of log D vs log fo_2 (Fig. 1) can be used to estimate the valence state of each element in the silicate liquid. By fitting the data linearly, the valence state can be derived from the slopes of the fitted lines. Our data yield very plausible values, e.g. 5^+ for Ta and 1^+ for In.

In Fig. 2 (A – C) the partition coefficients for the entire investigated P and T range are presented for Si, Ta and In. At the lower T of 2100°C, an increase in pressure from 6 to 20 GPa has little or no affect on the partitioning behaviour of these three elements, especially if the magnitudes of the uncertainties are taken into consideration.

At pressures of 18-20 GPa, temperature also has little or no effect on the behavior of Ta and In (Fig. 2 B, C); a similar observation has been made for Ga and Zn. However, for Si (Fig. 2 A) temperature has a significant effect on the geochemical behaviour (as observed previously [4]) with the partition coefficient increasing by at least one order of magnitude when the temperature is raised from 2100°C to to 2250 - 2400°C. But even at T > 2100°C (P ~20 GPa) Si is still less siderophile than Ta which would therefore have been extracted from the mantle by a core-forming iron alloy.

An interesting observation for In (Fig. 2 C) is that it behaves as a siderophile element even at the highest oxygen fugacities. This indicates that the observed depletion of In in the Earth's mantle could be partly the result of core formation, in addition to volatility

Conclusions: Our new experimental data on metal-silicate partitioning of the nominally lithophile elements Ta, Ga, In and Zn in the pressure range 6 - 20 GPa and temperature range 2100 - 2400 °C show that at low redox conditions they become siderophile and that pressure and temperature have little effect on their geochemical behaviour. For Si, our data show that its partitioning behaviour depends more on temperature than on pressure and that over a broad redox range of low redox values it is much less siderophile than Ta, for example. Therefore Si is unlikely to be a major light element in the core, at least on the basis of metal-silicate equilibration at P < 25 GPa, because at such conditions Ta would have also been strongly depleted from the mantle, which is contrary to geochemical observations.

References: [1] Wänke H. (1981) *Phil. Trans. R. Soc. London, 303, 287-302*. [2] O'Neill H. St. C (1991) *Geochim. Cosmochim. Acta, 55, 1159-1172*. [3] Allègre C. J. et al. (1995) *EPSL*, 134, 3–4, 515-526. [4] Gessmann, C.K. et al. (2001) *EPSL*, 184, 367-376.